Characteristics of Cloud-Nucleating Aerosols in the Northwestern Pacific Ocean

Project Summary

The indirect effect of aerosols on the radiative properties of clouds is potentially of similar magnitude, but has a larger uncertainty, than the direct aerosol effect. This project will collect and utilize experimental data to characterize the properties of the aerosols actually interacting with clouds and their effects on cloud microphysical and radiative properties. An airborne counterflow virtual impactor (CVI), which separates droplets from interstitial aerosol within a cloud, will be used to sample clouds in the ACE-Asia region. Once sampled, droplets will be evaporated within a moving gas stream. The residual nuclei will then be analyzed by various techniques. These include optical counting and sizing, electron microscopy, cloud condensation nuclei spectrometry, and thermal-optical analysis for elemental and organic carbon content.

Characteristics of aerosol particles sampled below clouds will be compared with residual nuclei extracted from cloud droplets to assess which particles act as cloud condensation nuclei. In particular, the relative importance of sulfate, elemental and organic carbon, sea-salt, and soil-dust will be evaluated in order to determine which particle types participate in cloud processes in polluted regions. The critical supersaturation spectra of the ambient particles and residual nuclei will also be analyzed. These data will be integrated with cloud microphysical data to evaluate the impact of anthropogenic aerosols on the microphysical and radiative properties of clouds in this region.

Project Description

1. Introduction

Of critical importance in predicting climate change are the indirect effects of aerosol particles on clouds; that is, how added particles act as cloud condensation nuclei (CCN) and subsequently may affect the radiation budget through changes in cloud albedo (Twomey, 1977[1]) and lifetime (Albrecht, 1989[2]). Our limited knowledge of these processes severely handicaps our ability to understand radiative forcing of anthropogenic aerosols, since the uncertainty due to aerosol effects on clouds is exceedingly large (Charlson et al., 1992[3]). This problem, although difficult, needs to be addressed with multiple approaches until a comprehensive understanding of the controlling factors emerges.

Measurements have demonstrated that aerosol particles can have a large influence on cloud radiative properties. For example, ship effluents often increase the albedo of overlying stratus clouds due to increases in droplet concentrations (Radke et al., 1989[4]), and similar effects have been observed downwind of industrial areas (e.g., Fitzgerald and Spyers-Duran, 1973[5], Twohy et al., 1995[6]). Leaitch et al. (1992[7]) compiled data from a series of flights in the northeastern United States and Canada and developed some positive relationships between aerosol number and droplet number. Likewise, Hudson (1983[8]) established relationships between CCN number and droplet number in stratus clouds. Some evidence for indirect effects of aerosols on cirrus clouds has even been presented (Sassen et al., 1995[9]).

Thus, indirect aerosol effects are recognized as important, but they are still poorly understood. The chemical heterogeneity of the anthropogenic aerosol and its interaction with the background aerosol makes simple parameterizations inadequate. Emphasis to-date has been on understanding sulfate aerosol effects, but other aerosol types, for example, organics and sea-salt, are also likely to be important in cloud formation. Limited experimental studies suggest that organic aerosols can act as cloud condensation nuclei (Novakov and Penner, 1993[10]; Facchini et al., 1999[11]). Recent modeling (O'Dowd et al., 1999[12], Ghan et al., 1998[13]) suggests that in cases of high to moderate windspeeds, the presence of sea-salt may dramatically influence the ability of sulfate to affect the microphysical, and therefore the radiative, properties of marine clouds. Applying these limited studies and our understanding of the non-linear, multistep physical processes governing cloud lifecycles to general circulation models (GCMs) is extremely difficult.

2. Scientific Questions

The Aerosol Characterization Experiment (ACE-Asia; http://saga.pmel.noaa.gov/aceasia/) is designed to study both the direct and indirect effect of aerosol particles on climate. The indirect effect of aerosols on the radiative properties of clouds is potentially of similar magnitude, but has a larger uncertainty, than the direct aerosol effect (IPCC, 1995[14]). While the ACE-Asia community is interested in both the direct and indirect effects of aerosol particles on climate, current plans call for the C-130 to focus primarily on aerosol measurements in March/April 2001. As proposed, much of the in-cloud flying would be performed by the Airborne Research Australia (ARA) King Air. The planned focus of the King Air measurements will be on the interaction between aerosol particles and clouds, including cloud processing of the aerosol, and effects of aerosol on clouds (Dr. S. Siems, personal communication). A second campaign in 2003, possibly with the C-130, would include more cloud measurements. It is uncertain, however, whether the 2003 phase of the project will be funded. Also, the King Air has limited range and payload capacity, and will have less aerosol instrumentation, than the C-130. Due to the great importance of the problem of the indirect effect, we propose here additional in-cloud measurements aboard the C-

130. Coordinated aircraft flights in the vicinity of fronts are already anticipated, and final flight plans will be influenced by the specific interests of the funded PIs. This, and the fact that the low-level cloud amount during this season is high (30 to 40%), promotes optimism that considerable C-130 flight time in cloud will be possible. While we have been invited to participate on the ARA King Air, some additional funds would be required (Dr. J. Jensen, CSIRO, personal communication). This is mentioned here as a possibility as a backup platform. The measurements proposed here are entirely complementary to the ACE-Asia objectives.

An airborne counterflow virtual impactor (CVI), which separates droplets from interstitial aerosol within a cloud (Noone et al., 1988[15]; Twohy et al., 1997[16]), will be used to sample clouds in the ACE-Asia region. Once sampled, droplets will be evaporated within a moving gas stream, and the residual nuclei* will be analyzed by various techniques, including optical sizing, electron microscopy, and thermal-optical analysis of elemental and organic carbon. The specific scientific questions we aim to study are:

Question A) *Which particle types are preferentially incorporated into clouds in this region? In particular, what are the relative roles of sulfate, sea-salt, soil-dust, elemental, and organic carbon?*

While models of cloud nucleation and growth are numerous, few measurements of particles actually incorporated into clouds exist (liquid cloud water samples don't allow analysis of individual droplet nuclei). ACE-Asia provides an opportunity to assess interactions of virtually all aerosol types with clouds, both near the heavily polluted source region and over a large region downwind.

The ACE-Asia sampling region will encompass eastern Asia and the northwestern Pacific Ocean between about 20° and 50° N latitude. The aerosol plume emanating from China and nearby countries will be a complex chemical soup, with sulfate, nitrate, and carbonaceous aerosol from industry mixed with soil-dust from desert regions and sea-salt from the ocean. Since more coal and biomass is burned in Asia than in Europe and North America, large quantities of carbonaceous aerosols (both elemental carbon, EC, and more complex organic species, OC) are produced in this region. During the springtime, dust storms occur frequently. Even these large particles can be transported long distances by the prevailing winds over the Pacific Ocean, where they interact with cloud systems. Figures 1 and 2 show how this interaction can result in dust being carried all the way across the Pacific to the western United States. Since dust particles are relatively large and can obtain a soluble coating over time (Dentener et al., 1996[17]), they may be effective CCN.

* The particles measured downstream of the CVI inlet after droplet evaporation will be called "residual nuclei" here, although in some cases, they may contain substances added to the actual cloud droplet nucleus after droplet formation, e.g., through chemical reactions, coalescence, or other in-cloud processes. Because particles are typically recycled through clouds many times before their removal from the atmosphere, these particles sampled by the CVI would also be potential CCN on their next passage through a cloud. Also, volatilization of droplets at 50°C is expected to remove some nitrate from the droplets, but should have little impact on the other species of interest here.

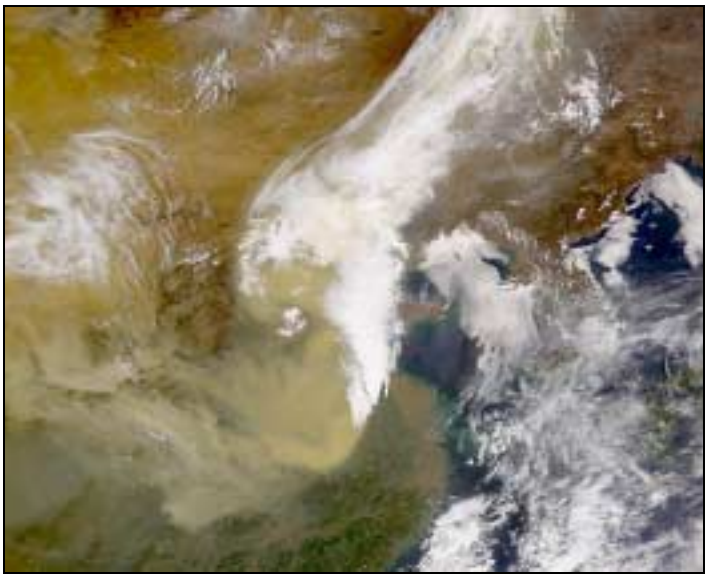

Figure 1. Figures 1 and 2 show the development of a large dust storm in China and its interaction with a meteorological system. In this image (April 16, 1998), the bright tan cloud near the coast is the center of the storm, being pushed by a frontal system. The atmospheric circulation around a low-pressure system entrained the dust from the storm and carried it far out into the Pacific Ocean. Images provided by the SeaWiFS Project, NASA/Goddard Space Flight Center and ORBIMAGE.

Figure 2. On April 25, dust from the event shown in Figure 1 reached the west coast of North America. The dust is visible in the clouds at the center of the left edge of the image, and as streaks of light brown haze over Cape Mendocino on the California coast. Images provided by the SeaWiFS Project, NASA/Goddard Space Flight Center and ORBIMAGE.

Sea-salt aerosol is also likely to be important to cloud formation in this region. For example, even in the polluted Indian Ocean, Satheesh et al. 1998[18] observed that the contribution of sea-salt to the total aerosol could be substantial and varies with surface windspeed. During the 1999 IOP of the Indian Ocean Experiment (INDOEX), sea-salt mass concentrations were generally low relative to the total aerosol. However, in preliminary analysis of INDOEX samples, sub-micron sea-salt particles were found be one of the dominant cloud nucleating aerosol types, even in polluted clouds (Twohy et al., 2000[19]). Because of their high solubility and relatively large size, sea-salt particles are exceptionally fine cloud condensation nuclei. In addition, they are likely to react chemically and form internally mixed particles with sulfate. This is expected to limit the tendency of sulfate to form new aerosol particles, potentially reducing the indirect effect of anthropogenic sulfur emissions (Figure 3). Cloud chemistry may also be dramatically impacted by the alkalinity of sea-salt (e.g., Twohy et al., 1989[20]).

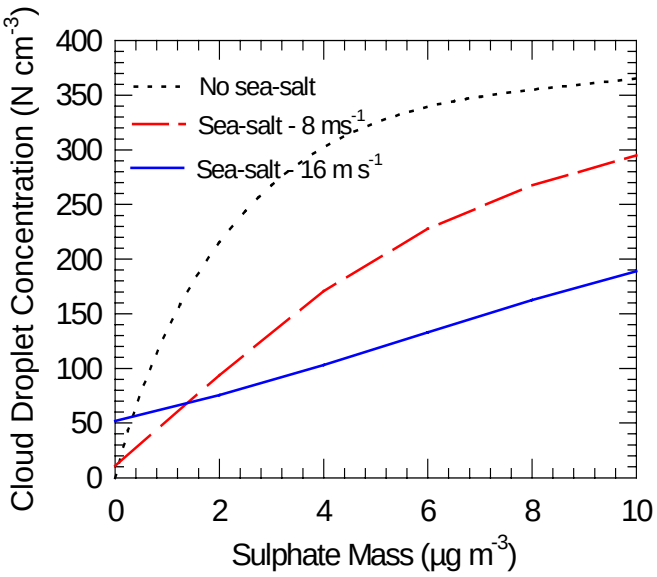

Figure 3. Predicted cloud droplet number concentration as a function of sulfate mass concentration for scenarios with and without sea-salt present. Sulfate condenses on existing sea-salt particles when they are present, reducing the potential contribution of sulfate to CCN number. Figure courtesy of Dr. C. O'Dowd.

Mineral and carbonaceous aerosols may also participate in cloud formation. Since soil-dust often has high alkalinity, it can acquire a sulfate or nitrate coating through uptake and reaction with SO_2 or nitric acid (Dentener et al., 1996[17]). As a result, soil-dust may have similar effects to sea-salt in terms of moderating the indirect effect of sulfate and nitrates on cloud droplet number concentration. Recent research (Novakov and Penner, 1993[10]; Facchini et al., 1999[11] has shown that organic aerosols may be important in cloud formation and chemistry, although the mixing state (internal vs. external), and effect of these aerosols on cloud number concentration is highly uncertain. Finally, in heavily polluted environments, elemental carbon may have important effects on cloud radiative properties by enhancing absorption within the cloud layer (Twohy et al., 1989[21]). Ackerman et al. (2000[22]) have proposed that this may heat the layer to the point where cloud lifetime is reduced (yet another potential indirect effect!).

Our main aim in ACE-Asia will be to determine which of these myriad aerosol types, especially the anthropogenic ones, are most important in cloud formation. In addition, aerosol transformations within cloud (e.g., sulfate production, coagulation) can be studied by the mixing state and chemical composition of the individual cloud residual particles. The possible effect of these processes on CVI data and interpretation is discussed at length in Ogren and Charlson (1992[23]).

The chemical and physical properties of the cloud nuclei can be used to calculate their critical supersaturation, S_c. The S_c is determined by the size and composition of the particle and is related to the number of soluble ions within a particle; larger, more soluble particles will have lower S_c values than smaller, less soluble particles. Particles that have S_c values less than the supersaturation actually reached within a cloud form activated cloud droplets if given sufficient time for growth (Squires, 1952[24]), while those with higher S_c's remain as smaller unactivated droplets, or haze droplets. This simple relationship can be complicated, however, in actual clouds in the atmosphere. The degree to which clouds can be described by simple adiabatic models, and which processes may act to change cloud microphysical properties, can be determined by measurements of the S_c spectrum of cloud residual nuclei. If we adequately understand cloud nucleation and lifecycle, cloud model predictions of which particles are incorporated into clouds and their subsequent transformations should match our measurements. Additionally, if our chemical and critical supersaturation measurements are adequate, then critical

supersaturations calculated from the chemical and physical properties of the droplet residual nuclei should also match*.

Question B) *What is the impact of the cloud nucleating aerosols, in particular anthropogenic aerosols, on the microphysical and radiative properties of clouds in this region?*

Using satellite observations, clouds in areas of the globe which are polluted have been shown to have smaller drop sizes and increased albedos than less polluted areas (Han et al., 1994[25]; Wetzel and Stowe, 1999[26]), which is the essence of the indirect (Twomey) effect. In-situ observations have also confirmed that increased aerosol concentrations can increase droplet number and decrease droplet size (Leaitch et al., 1992[7]; Martin et al., 1994[27]; McFarquhar and Heymsfield, 2000[28]). However, the relationship between aerosol number and droplet number is non-linear, and varies with location. Figure 4 shows that the effective radius of low clouds along the northeastern Asian coast, where aerosol optical depth is high, is substantially lower than for similar clouds in the central Pacific.

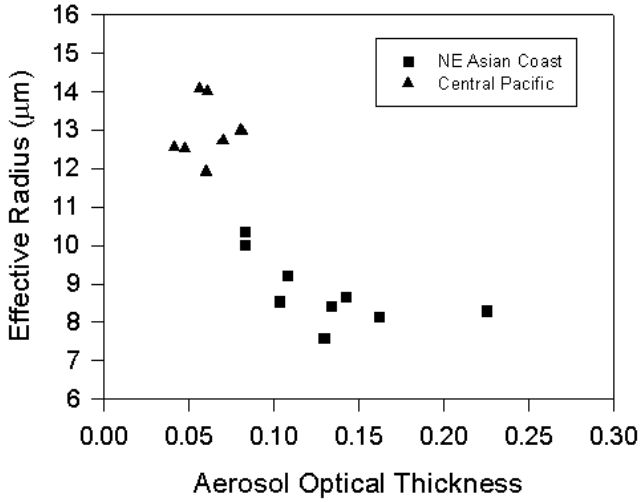

Figure 4. Regional averages of cloud droplet effective radius and aerosol optical thickness in July, for nine non-volcanic years during 1981-1994. Measurements are from the NOAA AVHRR satellite, with each point representing a 110 km^2 grid cell. From Wetzel and Stowe (1999[26]), courtesy of the authors.

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differences in microphysical forcing. For example, droplet concentrations are expected to be higher in regions with high number concentrations of sulfate aerosol, which has high solubility and low S_c, than in regions with similar number concentrations of elemental carbon, with low solubility and high S_c. Thus measurements of droplet nuclei size, composition and S_c, as proposed here, are important to include with simple measurements of aerosol and droplet number and size.

Table 1 shows preliminary data from the INDOEX experiment (Twohy et al. 2000[19]), taken from the NCAR C-130 in small cumulus clouds. Various properties of the clouds or cloud droplets are presented in blue, while properties of the below-cloud aerosol or droplet nuclei from the CVI are in black. Four cases have been studied in detail, ranging from a clean Southern Hemispheric case to a heavily polluted case near India.

* The conditions inside a CCN instrument do not simulate exactly what occurs in a natural cloud, so it is possible that particles acting as CCN in nature do not act as CCN inside an instrument, and vice-versa. These comparisons between chemical composition, size, and S_c should help to evaluate the veracity of the CCN measurements.

Table 1. Characteristics of Clouds Sampled During the Indian Ocean Experiment

	Updraft $m\ s^{-1}$	Drop N_d[(a)] cm^{-3}		LWC[(b)] $g\ m^{-3}$	MVD[(c)] μm	N_p[(d)] cm^{-3} %		CCN[(e)] S_c	OPC[(f)] diam, μm
	max	mean	max	mean	mean	mean	drops sampled	median	mean
CLEAN									
AMB 990324	-	-	-	-	-	186	-	0.15	0.19
CLD 990324	0.85	56	95	0.089	16.6	68	121%	0.12	0.18
Mod. CLEAN									
AMB 990220	-	-	-	-	-	335	-	0.15	0.20
CLD 990220	1.01	116	198	.093	15.0	68	72%	0.15	0.22
POLLUTED									
AMB 990321	-	-	-	-	-	1592	-	0.16	0.18
CLD 990321	0.90	137	239	0.060	11.9	44	32%	0.07	0.22
POLLUTED									
AMB 990227	-	-	-	-	-	2026	-	0.22/0.10	0.21
CLD 990227	1.4	167	306	0.12	13.9	122	73%	0.04	0.25

[(a)] droplet number from FSSP-100
[(b)] liquid water content from King hot-wire probe
[(c)] Mean volume diameter from FSSP-100
[(d)] CN concentration (under these circumstances, similar to accumulation-mode number concentration)
[(e)] CCN active at 1.0% S_c, measured by DRI CCN spectrometer
[(f)] dry mean diameter (lognormal) from LAS-AIR 1001 optical particle counter (> 0.1μm diameter). Particles below OPC detection limit, but measured by the CNC, will be included in final analysis and may decrease mean diameters, but not the sense of these relationships.

Droplet concentrations (N_d) are overall rather low, reflecting the relatively low updrafts and frequent entrainment and mixing of dry air occurring within these clouds (most only a few hundred meters in diameter). Droplet sizes are larger for the clean cases, as suggested by Twomey (1977[1]); however the influence of dynamics is apparent in the characteristics of the most polluted case (large updraft velocity, relatively large liquid water content, and medium-size droplets). Droplet concentrations are correlated with particle concentrations (black N_p), although the non-linearity in this relationship is apparent. For the cleaner clouds, the maximum droplet concentrations are 50-60% of the available particle number concentrations, while for the polluted clouds, only about 15% of the particles apparently act as droplet nuclei (at least this percentage has survived by the time these clouds were sampled). The percentages listed in blue under N_p represent the percentage of droplet number sampled by the CVI, relative to the FSSP. (The small cloud extent meant that different parts of the cloud were sometimes sampled by the FSSP and CVI, so percentages larger than 100% occasionally occured). Most of the droplets in the cloud were actually collected by the CVI, except for the third case, when the droplets were so small that some were below the CVI cut size of about 8 μm diameter. Note the droplet diameters given in the table are median volume diameters, not mean diameters, which were much smaller.

Comparison of the properties of the below-cloud aerosol and droplet nuclei can elucidate which of the ambient aerosol are acting as droplet nuclei under different situations. In the clean clouds, the properties (both median S_c and mean size) of the ambient and in-cloud aerosol are similar. This suggests a relatively uniform aerosol with most particles able to act as potential nuclei, and a high fraction which actually nucleate droplets. In polluted clouds, there are stronger differences between ambient and in-cloud aerosol, indicating that not all of the ambient particles are suitable CCN under these conditions. Droplet nuclei

have much lower median S_cs, and are larger, as expected by simple theory. However, differences between the S_cs are greater than differences between particle size, and may indicate preferential nucleation of particles with higher water solubilities[2]. Electron microscope analysis of both ambient and droplet nuclei samples is ongoing, and will help to determine which pollutant particles are acting as additional CCN, and just as importantly, which are not. Complete details of the CCN spectra and size distributions will also be utilized in the continuing analysis.

In INDOEX, very small cumulus clouds were sampled. Due to the high pre-existing aerosol optical depth and the limited spatial coverage of the clouds, little radiative forcing due to clouds was observed. In ACE-Asia, we expect to encounter thicker, more extensive cloud fields, which are more likely to have radiative impact. A higher incidence of soil-dust is expected in the ACE-Asia aerosol, and elemental and organic carbon detection will be added to the droplet nuclei measurements.

3. Field Experiment

Stratus and cumulus clouds downwind of the China will be sampled by both the NCAR C-130 and the ARA during March and April of 2001. The C-130 will carry a broad range of radiation, aerosol and cloud physics sensors, utilizing both in-situ and remote techniques. Along with radiometers and Particle Measurement Systems (PMS) optical probes for aerosol and cloud size distributions, numerous cabin-mounted aerosol measurements and an aerosol backscatter lidar will be included. While actual instrumentation will depend on which user proposals are funded, anticipated ambient aerosol measurements include complete size distributions, light scattering and absorption coefficients, electron microscopy, single-particle mass spectrometry, and filter and impactor sampling for inorganic ions, minerals, organics and elemental carbon. These instruments will sample air brought into the cabin through new porous diffusing inlets, designed to maximize transmission of coarse-mode aerosol particles like soil-dust and sea-salt.

We propose to add a CVI payload to the aircraft measurement package. Within the CVI inlet, cloud droplets larger than about 8 μm diameter will be separated from the interstitial aerosol and impacted into dry nitrogen gas. This separation is possible via a counterflow stream of nitrogen out the CVI tip, which assures that only cloud droplets are sampled. Because droplets in a sampling volume of about 200 l min^{-1} are impacted into a 10 l min^{-1} sample stream, concentrations within the CVI are enhanced by a factor of about 20. The non-volatile residual nuclei and water vapor remaining after droplet evaporation (at 50°C) will be simultaneously sampled downstream of the inlet with an number of different instruments (Figure 5).

[2] The possibility of in-cloud chemical reactions, which can increase the soluble material in particles, will also be considered, although the ambient aerosol sampled in INDOEX was already substantially aged and processed.

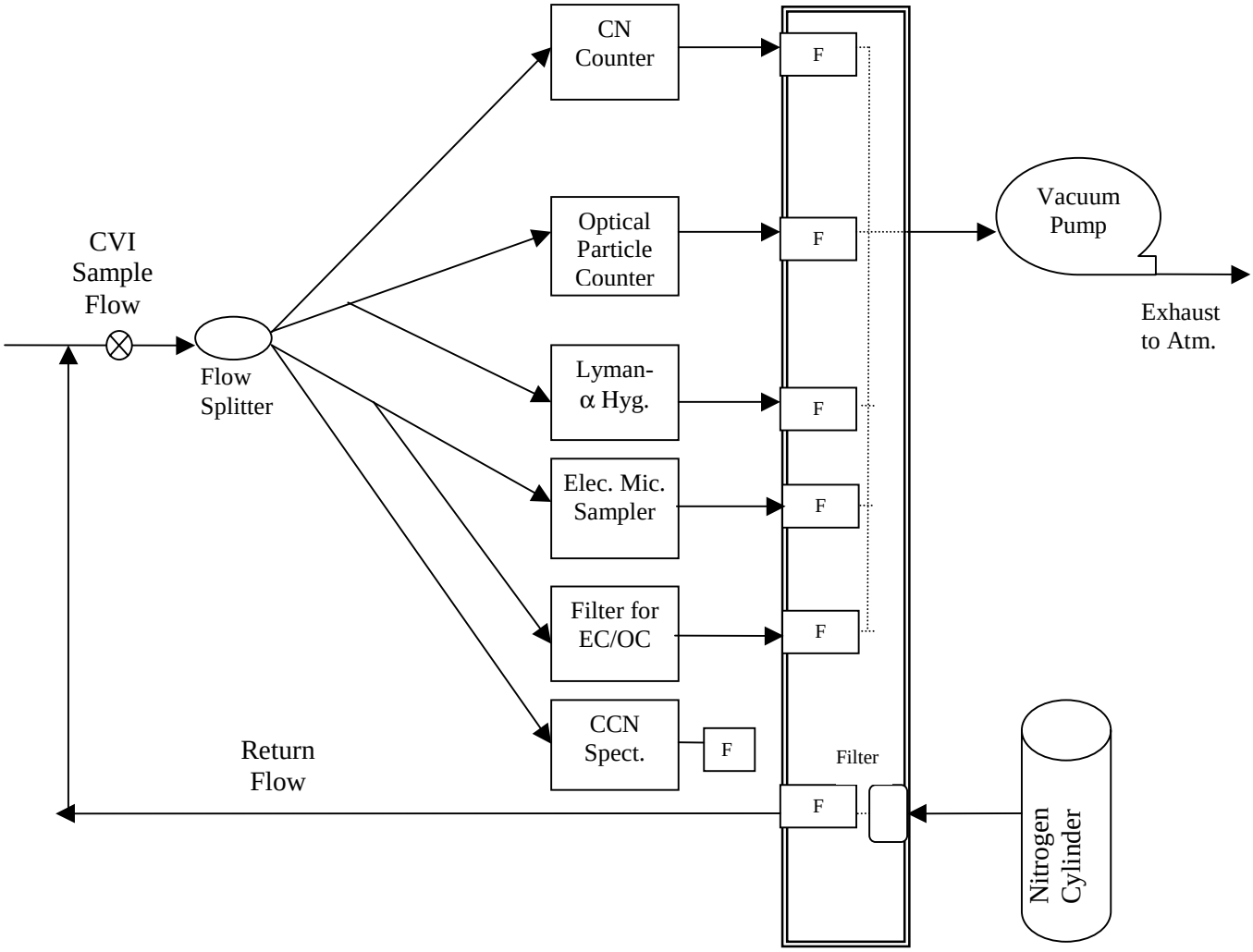

Figure 5. Flow diagram of CVI components for INDOEX. "F" denotes a mass flow meter or controller.

The total number of residual nuclei larger than 0.013 μm will be measured with a TSI 3760 condensation nucleus counter (CNC), from which droplet concentration sampled from the CVI is inferred. The water vapor will be measured by a Lyman-α hygrometer, so the liquid water content of the sampled droplets can be determined. The size distribution of residual nuclei will be measured in-situ with a PMS optical counter (diameter range size range 0.1 to >2.0 μm). The chemical properties of the residual nuclei as a function of particle size will be determined by automated scanning electron microscopy (SEM) and X-ray analyses of Anderson et al. (1996[29]), utilizing streaker samplers outfitted with 90 mm Nuclepore filters. Single-stage impactor samples for transmission electron microscopy (TEM) will also be collected. The actual CCN spectrum (critical supersaturation) of the residual nuclei will be measured in-situ with a fast-response CCN spectrometer (Hudson, 1989[30]). Although this is an extensive array of instruments to deploy simultaneously behind a CVI, a similar payload flew successfully during INDOEX.

For ACE-Asia, we propose to also use 1/3 of the sample flow to collect particles on quartz filters for element and organic carbon analysis via a thermal-optical technique (Birch and Cary, 1996[31]). At an ambient sampling volume of 200 l min^{-1} for the CVI, about 67 l min^{-1} equivalent will be available for the organic analysis. The detection limit of carbon analyzer is 0.23 μg C. To assess feasibility of this method,

we assume carbonaceous aerosol concentrations will be similar to those sampled in the INDOEX region of 0.5 to 15 μg C m^{-3} (Dr. Mayol-Bracero, personal communication) and that about 1/3 of the carbon mass is contained within droplets (Facchini et al., 1999[11]). Thus, sampling times of 1 to 20 minutes in cloud, depending on pollution level, should be sufficient to obtain usable samples. Transmission lines downstream of the stainless steel inlet will be modified to eliminate any possible organic artifacts. For ACE-Asia, we will not attempt size segregation or speciation of organic component due to the uncertainty in obtaining sufficient samples for analysis; this will be planned for future experiments. However, a simple measurement of the proportion of organic and elemental carbon within droplets will be very informative.

Assuming successful proposals, the chemical properties of individual ambient aerosol particles will be measured via electron microscopy by Dr. James Anderson, and organic and elemental carbon will be measured by Prof. Barry Huebert and Prof. Dr. Jian Yu. CCN spectra will be measured by Dr. James Hudson. These techniques and experimenters measuring ambient particles are the same as those being proposed for measurements of droplet nuclei behind the CVI. (Letters of support from Dr. Anderson and Prof. Yu are provided at the end of this proposal.) Ambient aerosol size distributions will be measured by Dr. Steve Howell and Prof. Antony Clarke (Clarke, 1991[32]), using a similar optical particle counter to that being used with the CVI. The size, composition, and cloud nucleating properties of the ambient aerosol therefore can be compared directly to corresponding properties of the residual nuclei actually present in clouds formed on that aerosol. While we have already established collaborations with these particular researchers, if other researchers with similar techniques are chosen for the ACE-Asia science team instead, we will seek collaboration with the new team members in order to keep the proposed payload intact.

4. Analysis of Residual Nuclei from Cloud Droplets

This section describes details of how the data and samples acquired in the field will be analyzed and used to answer the pertinent scientific questions.

a. Particle size distributions

Particle size distributions of the CVI residual nuclei will be constructed in two ways. First and most straightforward, data from the LASAIR optical particle counter and TSI condensation nucleus counter will be analyzed to produce a nine-channel size distribution. This will utilize the eight LASAIR channels, and the total CN concentration minus the total LASAIR concentration for the smallest size channel (the LASAIR samples only the larger particles, while the CNC samples smaller particles as well). Another particle size distribution will be obtained with the automated SEM results. This technique has a lower detection limit of 0.08 to 0.15 μm, depending on particle composition. While the LASAIR can obtain a single size distribution in six seconds, the SEM and OC/EC filters will require at least a one-minute cloud sample for adequate statistics. In order to compare results from the two techniques, LASAIR data will be averaged over the filter sample intervals. Since the CVI rejects ambient aerosol between clouds, residual nuclei size distributions can be obtained even if the clouds are small and patchy. After corrections for sampling conditions (see **e**, below), the two sets of nuclei size distributions will be compared with each other for consistency, and with ambient particle size distributions measured by Drs. Clarke and Howell.

b. Particle composition via SEM/TEM

The automated SEM analysis will provide size-dependent composition for several particle types, including sea-salt, sulfates, and soil-dust. Unlike bulk sampling methods, this technique produces information on individual particles, such as their size and composition and the degree to which they are

internally mixed (i.e., different chemical species present within a single particle). This type of analysis is critical in determining what particle types actually participate in cloud formation, and it can be extremely revealing. For example, using the CVI, Twohy and Gandrud (1997[33]) found that both mineral and metallic particles apparently can nucleate ice crystals in aircraft contrails, although these particle types were previously considered to be relatively unimportant. INDOEX results have verified the importance of sea-salt as CCN (Twohy et al., 2000[19]), and will show which anthropogenic particle types participate in cloud formation. The SEM technique to be used in this work is automated and can run continuously, so that much more data can be produced than by methods requiring a human operator. We plan to have the ACE-Asia SEM samples analyzed within a year of the project's conclusion.

More detailed chemical information can be obtained via TEM with energy dispersive spectrometry (Posfai et al., 1995[34]). However, since the TEM analysis requires an operator, it is more expensive and time-consuming; thus, only a subset of samples will be analyzed via TEM. This sample subset will be selected post-project in order to derive more information about the most promising cloud cases. The TEM analysis will supplement the faster SEM analysis by providing more information about both elemental carbon and nitrate within individual particles. Of particular interest is the degree of internal mixing of elemental carbon (EC) with sulfate, since sulfate coatings can make EC hydrophilic and more likely to act as CCN. When coupled with electron diffraction techniques, the crystalline structure of various minerals and salts can also be identified via TEM.

Dr. Anderson is proposing to participate in ACE-Asia under a separate proposal to NSF, and funds for analysis of CVI samples at Arizona State University are included there. Consolidation of the large quantities of data acquired by SEM, correction of the size distributions for sampling effects (see **e**, below) and comparisons of the data with ambient samples and with cloud microphysical properties are also covered through this proposal.

c. Aerosol critical supersaturations from CCN spectrometer

Complete CCN spectra will be constructed for droplet nuclei and corresponding ambient samples (usually below-cloud, although cloud-level and above-cloud measurements will be studied if available). Again, data will be averaged over the same time periods as the filter samples, to facilitate direct comparison of results. The latest mathematical inversions, for better CCN data quality (Dr. J. Hudson, personal communication), will be applied. For ease of comparison of all cloud cases, summary parameters, specifically mean number concentration and median S_c (and possibly a shape factor) will be compiled. The complete spectral information will be used to examine individual cases in detail, and for comparison with size distributions and composition data.

The CVI has been paired with this CCN spectrometer in previous experiments (Twohy and Hudson, 1995[35], Twohy et al., 2000[19]) to measure the critical supersaturation of droplet nuclei. In the first program, the larger cloud droplets in marine cumulus clouds were preferentially sampled, to investigate the effects of entrainment and mixing on cloud lifecycle. Despite the frequent mixing, the mean critical supersaturation of the droplet nuclei tended to be lower than that of the ambient aerosol. This reflects the preferential nucleation of the larger drops on larger, more soluble particles, which is expected from theories of adiabatic cloud formation. However, when details of the actual critical supersaturation spectra were examined, deviations from adiabatic theory could be observed, especially in the upper regions of the clouds where entrainment and mixing with ambient air had occurred. Studies like this are important to demonstrate where particles actually enter clouds, and when simple theories of cloud formation are insufficient. Comparisons of droplet nuclei and ambient CCN spectra from ACE-Asia will be used, in conjunction with composition data, to determine which anthropogenic aerosol particles act as CCN. Comparisons with theory will also be made in modeling studies, below.

d. Carbon analysis

Organic and elemental carbon mass in the droplet nuclei samples will be determined by thermal-optical analysis as in Birch and Cary[30]. In this method, the sample is heated to different temperatures, and the carbon volatilized at various temperatures is converted to methane for detection by a flame ionization detector. An optical feature is used to correct for pyrolytically generated EC (char), which reduces any tendency for artificially high EC results. Filter mass loadings will be converted to μg (EC or OC) m^{-3} air, for comparison with the ambient aerosol samples analyzed by the same technique. The proportion of EC and OC relative to each other, and the proportions which nucleate cloud droplets, will be determined. This information will be used to supplement the composition data from the SEM, for studying possible effects on the measured S_c spectrum, and for determining whether EC concentrations within droplets are large enough to produce radiative effects.

e. Sampling issues and corrections

Basic qualitative assessments of the nature of residual nuclei and general comparisons with nearby ambient particles can be made with the basic data set, with only simple corrections for the CVI enhancement factor mentioned earlier. However, quantitative assessments that specifically match characteristics of residual nuclei with characteristics of corresponding ambient particles require that deviations in the original particle distributions due to sampling biases be quantified, and corrected whenever possible. These sampling issues are time-consuming and are often omitted from aircraft studies, but can be significant (e.g., Huebert et al., 1990[36]). Through the analysis discussed below, we can be assured that differences observed between CVI and ambient samples are due to actual cloud processes, and not sampling conditions. Uncertainty values will be developed for all distributions, based on this information.

First, we consider the ambient aerosol samples collected, some with new porous diffusing inlets under development at Denver University. While these inlets with boundary-layer suction should reduce large particle losses due to flow separation, they are not expected to collect all particle sizes with equal efficiency. Results from efficiency testing later this year will be used to correct ambient samples collected with single particle methods. The OC/EC samples, which will not distinguish individual particles, will be obtained with a total aerosol sampler ("TAS", Prof. B. Huebert, personal communication). This technique will allow all aerosol mass to be collected, regardless of particle size.

Particle losses can occur in the lines between the sampling inlet and the detecting instrument due to impaction, sedimentation, and diffusion. While these processes can be minimized with proper sampling design, they cannot, in most cases, be eliminated entirely. These loss mechanisms are a function of particle size, and they can be calculated with reasonably accuracy based on existing theoretical and empirical studies (e.g., Reist, 1993[37]). The effect of changes in relative humidity during the sampling process (Howell and Huebert, 1998[38]), and of spreading of liquid particles on the SEM and TEM samples (e.g., Gras and Ayers, 1979[39]) must also be considered. Based on these factors, size-dependent corrections algorithms will be developed for the sampling configurations used for the ambient CCN, SEM/TEM, and optical size distributions, in order to correct the data used in this work.

Impaction and collection efficiency of the CVI has been studied both empirically and theoretically, with reasonable agreement between the different methods (Noone et al., 1988[15], Anderson et al., 1993[40], Lin and Heintzenberg, 1995[41], Laucks and Twohy, 1998[42]). The CVI cut size, or minimum size of droplet collected with 50% efficiency, is well characterized, with an uncertainty of only about 1 micron diameter. Some uncertainty in collection efficiency above the cut size, however, still exists due to the exclusion of droplet evaporation in impaction calculations. We plan to expand our current computational fluid

dynamics model of the CVI to include evaporation, as part of other NSF work. This information will be used to correct CVI data from ACE-Asia, if it turns out to be necessary.

5. Microphysical Measurements and Analysis

A series of microphysical measurements will be made in-situ on the C-130. Although details are not finalized, these are likely to include a full range of PMS optical probes to measure particles (about 0.3 μm to 1 mm) and hot-wire probes for liquid water content. We will work closely with Dr. Darrel Baumgardner of NCAR/RAF to assure that we obtain the highest quality microphysical information. Important quantities, such as liquid water content, droplet number concentration, drizzle concentration, and mean volume diameter of the ACE-Asia clouds will be summarized. These will be combined with the aerosol data to develop simple relationships such as those of Martin et al. (1994[27]), as well as the more complex ones shown in Table 1. Time series of aerosol and cloud properties will also be perused to examine smaller scale relationships (e.g., Twohy et al., 1995[6]), and the effects of aerosol gradients. Also, simple calculations (e.g., Leaitch et al., 1992[7]) will evaluate potential radiative effects of changes in cloud microphysics.

6. Modeling Efforts

Models with detailed cloud chemistry and microphysics can provide valuable information for understanding indirect climate forcing—for example, which aerosol types can be important in cloud formation (O'Dowd et al., 1999[12]), how gas and particulate partitioning may change due to cloud processing (Hegg, 1985[43], Hoppel et al., 1986[44], Lelieveld and Heintzenberg, 1992[45]), and even how cloud lifetime may be modified due to changes in the drop size distribution (Albrecht, 1989[2]). When substantiated by measurements, these models can be utilized to drive the development of new modules and to develop parameterizations useful for GCMs.

Several modeling groups have expressed interest in utilizing the size-dependent chemical information obtained with the CVI to test their models. At NCAR, the Model for Aerosol Process Studies (MAPS) is being developed by Dr. Susan Durlak. MAPS is based on a detailed aerosol model developed by Wexler et al. (1994[46]). Aerosol types in this model are divided into distinct size classes. This is necessary since chemical composition, solute concentration, and sulfate production are all expected to vary with cloud droplet size (Twohy et. al., 1989[20]). This model also includes detailed chemical information, including organic species and the effects of internally mixed particles. Although external aerosol mixtures or cloud processes are not currently included in MAPS, these improvements are expected to be complete by the ACE-Asia 2001 IOP (progress documented online at http://raf.atd.ucar.edu/~durlak/MAPShome.html).

Two other groups, led by Prof. Dean Hegg at the University of Washington and Dr. Colin O'Dowd at the University of Sunderland, have one-dimensional cloud models with simpler chemistry, but with cloud processes already included. These models will be particularly good for evaluating the importance of sea-salt aerosol, although the influence of more complex aerosol types (e.g., organics) may require further model development. These groups have both expressed an interest in collaborating on the use of the CVI data, along with the ambient aerosol data, to evaluate whether their models accurately predict cloud formation and processing of aerosol. Since this work should improve their cloud modeling capabilities and lead to better understanding of the factors controlling the indirect aerosol effect, we strongly endorse this use of the ACE-ASIA data. Although these modeling studies are not supported explicitly through this proposal, we will provide detailed, corrected chemical size distributions as input for the work of these scientists.

7. Integration of Data with Scientific Questions

This section summarizes how the proposed measurements and analysis will aid specifically in answering the scientific questions posed in the Section 2.

Question A) *Which particle types are preferentially incorporated into clouds? In particular, what are the relative roles of sulfate, sea-salt, soil-dust, elemental, and organic carbon?*

The single-particle chemical analyses will be used to determine the relative percentages of sulfate, sea-salt, and soil-dust in each sample. Some information on cloud processing will also be obtained, since quantification of how much of the chlorine in sea-salt is reacted to sulfate can be obtained. The relative roles of elemental and organic carbon in droplets will be obtained from the results of the thermal-optical analysis. Ambient and CVI samples will be compared and contrasted statistically, as well as on a case-by-case basis. Particle size distributions (from both the optical sensors and the electron microscope analysis) will also be an important part of this comparison, since cloud-nucleating ability is dependent on particle size as well as composition.

The critical supersaturation spectra of the ambient particles and residual nuclei will be compared statistically and on a case-by-case basis. Case studies will determine if the in-cloud aerosol follow the simple adiabatic relationship expected--i.e., that the particles with the lowest S_c preferentially nucleate into cloud droplets. Also, the CCN data will be compared to the size and chemical characteristics of the residual nuclei to determine if these two measurement types are consistent.

Question B) *What is the impact of the cloud nucleating aerosols, in particular anthropogenic aerosols, on the microphysical and radiative properties of clouds?*

Air trajectories and aerosol chemical measurements will enable us to determine the source, type, and concentration of anthropogenic aerosols in the region. Thermodynamic, aerosol, and cloud properties will be compiled into a data base available to interested scientists. Variations in these parameters will be studied via multivariate techniques such as principal component analysis (PCA[47]), in order to determine which variables are related and to help separate aerosol effects from dynamic effects on clouds.

8. Work Plan

In the first year (8 month term), data and samples will be collected, with both the PI and a graduate student participating in the field work. After the experiment, basic data from the CVI will be calculated and added to the NCAR/RAF aircraft data set (if we are funded for the C-130). These data include droplet nuclei number concentration and condensed water content. An overall quality check of all the CVI data will also be performed. Each cloud sampling period will be evaluated, documented, and priority cases will be selected. In the second year, correction algorithms required for various sampling conditions will be developed. It is also expected that the SEM/TEM analysis of ambient and residual nuclei will be performed at Arizona State University and the EC/OC analysis at the University of Hong Kong. Corrected CCN and size distributions, including chemical speciation, will be constructed, and comparison of the ambient and CVI samples and integration with cloud microphysical parameters will also occur in the second year. Presentation of initial results at a conference is also planned. In the final year, statistical relationships between the various parameters will be developed, and it is expected the results will be published in peer-reviewed journals such as JGR-Atmospheres.

Table 2 lists the various tasks required and the expected time required for completion in full-time months (PI=Principal Investigator; GS=Graduate Student).

Table 2. TASK	**Yr1 PI**	**Yr1 GS**	**Yr2 PI**	**Yr2 GS**	**Yr3 PI**	**Yr3 GS**
Field Phase, including preparations		1.0				
Case-selection, data quality checks	1.0					
Correct EM and optical size distributions			0.5	1.0		
Compile ambient vs. CVI comparisons-chemistry, size			1.0			
Correct CCN size distributions			0.5			
Compile ambient vs. CVI comparisons-CCN			1.0			
Statistical comparisons					1.0	
Finalize and write up results					2.0	1.0
TOTALS	**1.0**	**1.0**	**3.0**	**1.0**	**3.0**	**1.0**

9. Personnel

The PI, Dr. Cynthia Twohy, will perform most of the analysis described with the data collected during ACE-ASIA. A graduate student from Oregon State University's Atmospheric Sciences department will aid in the field work and analysis; this person is expected to arrive in Fall 2000 and work on the INDOEX data set as well. Dr. Twohy will oversee all the analyses, continue the collaborations with involved scientists at other institutions, and assure publication of final results. Dr. Twohy has served as instrument PI, project manager, or mission scientist in about 15 airborne research projects, and has over ten years experience analyzing various chemical and microphysical data from aerosols and clouds.

Several scientists plan to collaborate in this effort, and are key to its success. Dr. Jianzhen Yu (formerly with Prof. John Seinfeld) at Hong Kong University will analyze the CVI filter samples for OC/EC, as well as the ambient samples taken by other researchers. Dr. Jim Anderson at Arizona State University will collect and provide size-dependent composition using the electron microscope facilities at his university. Dr. Jim Hudson of Desert Research Institute will collect and provide the CCN data. Both Dr. Anderson and Dr. Hudson have extensive experience collecting and utilizing aircraft data. Microphysical and thermodynamic data from the aircraft will be provided by NCAR's Research Aviation Facility, with Dr. Darrel Baumgardner consulting on data quality issues. All these investigators have expressed a strong interest in utilizing the CVI to obtain data on cloud properties. Written letters of collaboration from Prof. Yu and Dr. Anderson are included as supplemental information.

10. Facilities and Equipment

The CVI is an existing instrument at NCAR's Research Aviation Facility. (The LAS-AIR optical particle counter is the only part of the payload required through this grant.) The PI has a laboratory at NCAR in which she can calibrate and test the equipment before installation. Extensive electron microscope facilities at Arizona State University will be utilized for the chemical analysis; the SEM is a JEOL model 5800 with full automation of the column, stage, and imaging systems. Energy-dispersive spectrometer (EDS) is used to acquire X-ray spectra. ASU also has several TEMs that can be used for chemical analysis, high-resolution structure imaging, and electron diffraction. The EC/OC analysis will be

performed at Hong Kong University of Science and Technology, where the Sunset carbon analyzer is already available. Computing facilities required for the work (two Dell PCs) are resident at Oregon State University.

11. Results from Prior NSF Support

The PI has an existing NSF grant, "Characteristics of cloud-nucleating aerosols and their effects on cloud microphysical and radiative properties in INDOEX". This is related and complementary to the work proposed here. The prior award number is ATM-9906903, for 35 months and $197,772.

This award covers analysis of CVI data from the Indian Ocean Experiment (INDOEX). Since this work began in August 1999, only early results are available. All the significant cloud sampling periods during INDOEX have been compiled and evaluated according to the quality of the data and utility for addressing the effect of aerosols on cloud microphysical and radiative properties. This resulted in a table of 21 cloud passes, with electron microscope samples, CCN data, and size distributions for the droplet nuclei collected for all cases. Ambient aerosol samples associated with each of these cloud passes were also identified. Four of these cases, two from the clean Southern Hemisphere and two from the polluted Northern Hemisphere, have already been evaluated, and were summarized in Table 1. A positive, but non-linear, correlation between aerosol number and droplet number was observed, and droplets were smaller in the polluted cases than for the clean cases.

The other important points relate to the measured sizes and critical supersaturation of the ambient aerosol vs. the droplet nuclei. Strong similarities were observed between the ambient aerosol and cloud nuclei for the clean cases, but large differences were apparent for the polluted cases. This suggests that a relatively uniform aerosol exists in the clean environment, with most particles able to act as potential nuclei. In the polluted clouds, however, particles with larger sizes and lower critical supersaturation are more likely to be incorporated into cloud. This indicates that not all of the ambient particles are suitable CCN under polluted conditions. Electron microscope analysis is only complete for one of each case types. Early results show a high percentage of sea-salt and agglomerated particles in the cloud samples, although other particle types are present, especially in the polluted case. Since it isn't presently known how representative these two cases are, more analysis is necessary before more definitive statements can be made.

The PI has presented these preliminary results at an INDOEX workshop in the Netherlands and at the Fall AGU meeting in California (Twohy et al., 2000[19]). She also plans to submit at least one paper for a JGR special issue on INDOEX in July.

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